Structural Disorder in a Dihydroxo-Bridged Fe(II)-Fe(III) Complex Revealed by XAFS Analysis
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Introduction: Dinuclear iron complexes containing an Fe_2O_2 rhomb are of interest as models of the structure and function of the active site of the hydroxylation protein of methane monooxygenase (MMOH). Recently, a mixed valence ($Fe^{II}Fe^{III}$) form of MMOH was structurally characterizing as containing a triply-protonated rhomb (i.e. one μ-OH and one μ-OH_2 bridging the iron atoms).[1] As part of an ongoing program at U. Southern Denmark to synthesize new models for MMOH, the dinuclear complex $[L_2Fe_2(OH)_2](ClO_4)_3 \cdot 3H_2O$ (**1**, L = *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine) was synthesized and crystallized and a structure was determined by X-ray diffraction. In the initial structure, the two iron atoms were related by symmetry, suggesting a delocalized mixed-valence complex ($Fe^{+2.5}Fe^{+2.5}$). We used X-ray absorption fine structure measurements of **1** to investigate whether the oxidation states of the iron atoms were truly delocalized.

Methods and Materials: 6 mg of **1** was ground with 100 mg of BN and packed into a 1.3 mm deep slot in aluminum sample holders. 1 mil 3M Kaptan tape was used to hold the sample in the slot. Data was collected at room temperature in both transmission and fluorescence modes using i0, i1 and iref gas ionization detectors and a Canberra 13-element(Ge) solid state detector. Data analysis and graphing employed "RCSEXAFSpackage" written for *Igor Pro* software and general methods that have been described previously.[2]

Results: The XANES (near-edge) spectra of iron complexes generally are shifted to higher energy (to the right, when graphed) on going from Fe^{II} to Fe^{III} complexes. An intermediate shift is expected when the oxidation state of each iron is +2.5, and this has been observed in a recent study of a carboxylate-bridged mixed-valence dimer.[3] But in the case of **1**, the XANES features (and particularly the 1s→3d transition at ca. 7113 eV) are broadened relative to the features in Fe^{II} and Fe^{III} complexes. Spectral simulation shows that the observed XANES for **1** can be almost exactly simulated as equal 50% contributions from the XANES of an iron(II) complex and an iron(III) complex. This indicates that the iron atoms have localized valences of +2 and +3 on the X-ray time scale.

The localized-valence conclusion from XANES was, however, in conflict with the equal Fe-O distances seen in the crystal structure, since Fe^{II}-O bond lengths tend to be 0.1 - 0.2 Å longer than Fe^{III}-O lengths. The EXAFS of **1** could be fit with 4 (per Fe dimer) Fe-O bonds at 1.97 Å and 8 Fe-N bonds at 2.21 Å (within 0.02 Å of the crystallographic averages). However, the refined σ^2 for the Fe-O shell was unusually large (0.018 $Å^2$, compared with 0.006 $Å^2$ for the Fe-N shell). This indicated there were at least two different equilibrium Fe-O bond lengths separated by over 0.1 Å. A better fit (even after correcting for the additional refined parameter) was obtained by refining 2 Fe-O distances each to 1.90±0.03 and 2.12±0.08 Å. The refined σ^2 for these Fe-O shells was 0.004 $Å^2$, typical of what we have obtained for compounds with only vibrational disorder in the bond lengths. The combined results from XANES and EXAFS analysis indicate that the iron atoms in **1** are localized in their valence on the X-ray time scale. Since the same time scale applies to X-ray diffraction, the apparent equivalence in Fe-O bond lengths in the crystal structure is ascribed to structural disorder.

Based on these results, the diffraction data of **1** was re-fit using two half-occupancy isotropic oxygen atoms instead of the single anisotropic bridging O atom. The R_w was identical (0.044) for the two models to the electron density, but the disordered model is obviously preferred because it explains the EXAFS and XANES results. In the disordered model, the averaged distances ascribed to Fe^{III}-O (1.89 Å) and to Fe^{II}-O (2.07 Å), as well as the Fe-Fe distance (2.95 Å) are within the uncertainty ranges for these parameters established by EXAFS analysis. The results of this study have been submitted for publication.[4]

Conclusions: An $Fe^{II}(\mu$-OH$)_2Fe^{III}$ complex has been synthesized and has localized valence based on X-ray spectroscopy (XAFS). The conclusions from XAFS were used to correctly model the X-ray diffraction data.

References:
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